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***N*-酰胺基硫脲类受体分子的设计合成和阴离子识别**

Design and Synthesis of *N*-Amidothiourea-Based Neutral Receptors for Anion Recognition

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N-酰胺基硫脲类受体分子的设计合成和阴离子识别

摘 要

分子识别是超分子化学研究的核心内容之一，包括阳离子、阴离子和中性分子的识别。识别作用力主要系弱的分子间作用力，如库仑力、范德华力、氢键、离子对、疏水亲脂作用等。阳离子识别研究发展较快并已渐趋成熟，而阴离子识别的发展相对较为迟缓，亟待丰富和发展新型识别体系。由于自然界中生物体内的阴离子识别主要通过多重氢键协同作用得以实现，基于氢键作用的中性受体分子成为阴离子受体分子发展的重要趋势之一，其中以（硫）脲基团为氢键结合位点的中性受体分子备受关注。

（硫）脲类受体分子设计主要有两个方面，一是通过改变硫脲 NH 上的烷基或芳基来调节 NH 质子酸性，提高硫脲与阴离子的结合能力；但酸性过高时，阴离子存在下可能发生脱质子过程，所以取代基的调节能力有限。二是多个（硫）脲或（硫）脲与其它结合位点协同作用，构建有利于阴离子结合的立体结构，籍多重氢键的协同作用来提高阴离子结合能力，达到选择性识别阴离子的目的，但此类受体分子结构复杂，合成较为困难。

实验室前期工作发现，相较于二苯基硫脲，在不提高硫脲 NH 质子酸性的前提下，*N*-苯甲酰胺基-*N'*-苯基硫脲与阴离子的结合常数较二苯基硫脲提高了两个数量级，是一类具有发展潜力的阴离子受体分子。研究发现 *N*-苯甲酰胺基-*N'*-苯基硫脲分子中，*N'*-苯基上取代基影响受体分子与阴离子的结合，而 *N*-苯甲酰胺基上取代基的改变对受体分子的阴离子结合常数影响不大。因此，本论文中将 *N*-苯甲酰胺基中的芳香苯基替换为脂肪烷基，设计合成了一系列 *N*-（取代乙酰胺基）-*N'*-（取代苯基）硫脲，使 *N*-酰胺基硫脲基团进一步拓展，成为一类应用前景广泛的阴离子结合基团。论文共分五章。

第一章概述了近年来以硫脲基团为结合位点的中性阴离子受体分子的研究进展，在实验室前期相关工作的基础上提出论文设想。

第二章详细叙述了论文中所涉及的受体分子的合成和结构鉴定。包括各种取

代的 *N*-乙酰胺基-*N'*-苯基硫脲和 *N*-苯甲酰胺基-*N'*-苯甲酰基硫脲, 共约三十种化合物。

第三章: 将 *N*-苯甲酰胺基-*N'*-苯基硫脲拓展为 *N*-(取代乙酰胺基)-*N'*-(取代苯基) 硫脲, 研究了受体分子的吸收光谱对阴离子的响应。考察取代基的改变对受体分子与阴离子结合能力的影响, 说明酰胺基硫脲作为一种新型的阴离子结合单元不仅可与芳香酸耦合, 也可与脂肪酸相耦合; 且在硫脲 NH 质子酸性相对较低的条件下与阴离子结合能力更强。核磁滴定实验表明: 当苯环上取代基的拉电子能力小于 *m*-CF₃ 时, 受体分子与阴离子作用为氢键作用; 当取代基为 *p*-NO₂ 时, 受体分子与阴离子间 (F⁻ 和 CH₃CO₂⁻) 未经过氢键结合而直接发生脱质子过程。与不含酰胺基 NH 的模型化合物比较, 说明受体分子 *N*-乙酰胺基-*N'*-苯基硫脲与阴离子间以氢键结合后, 受体分子-阴离子结合物中所形成的氢键网络有助于受体分子中 NH 质子的稳定, 不利于脱质子过程的发生。由于与阴离子间强的结合能力和氢键网络的形成, 受体分子 *N*-乙酰胺基-*N'*-苯基硫脲可实现在含 10% 水的乙腈混合溶剂中的阴离子识别。

第四章: 以 *N*-酰胺基-*N'*-苯基硫脲为阴离子结合单元, 萘基和芘基为荧光发射基团, 应用相对较长的连接臂合成了 PET 型阴离子受体分子 *N*-萘乙酰胺基-*N'*-苯基硫脲 (**6**) 和 *N*-芘丁酰胺基-*N'*-苯基硫脲 (**7a-c**)。通过考察受体分子吸收光谱、荧光光谱和核磁位移对阴离子的响应, 发现与以简单的硫脲基团为结合单元的受体分子 **T5** 相比, *N*-酰胺基-*N'*-苯基硫脲有较高的氧化电位 E_{ox} , 但在乙腈中与阴离子间有较高的猝灭常数 ($10^5 \text{ mol}^{-1} \text{ L}$ 数量级) 和灵敏度。与阴离子结合之后, 受体分子 **7** 中电子给体部分的氧化电位显著降低。这一结果表明作为电子给体, *N*-酰胺基-*N'*-苯基硫脲在构建基于 PET 型的阴离子识别受体分子时较硫脲基团更为有利, 可使阴离子结合的信号得以放大。由于 **7c** 在乙腈中表现出对阴离子高的结合能力, 在 8% 的乙腈-水混合溶液中对 CH₃CO₂⁻ 也表现出较高的光谱响应和灵敏度。

第五章: 已知 *N*-苯甲酰基-*N'*-苯基硫脲中存在强的分子内氢键, 无法与阴离子结合, 其吸收光谱和荧光光谱对阴离子无响应。在 *N*-苯甲酰基-*N'*-苯基硫脲中引入酰胺基团构建的受体分子 *N*-苯甲酰胺基-*N'*-苯甲酰基硫脲中同样存在分子内氢键, 却能对阴离子产生有效的光谱响应, 受体分子与阴离子间结合常数与

N-苯甲酰基和 *N'*-苯甲酰基中苯环上取代基的 Hammett 常数变化均无关。结果表明受体分子与阴离子结合时发生分子内氢键的断裂,同时,发生包含苯甲酰胺基团的旋转和 N-N 构型的扭转,后者使硫脲基团与 *N*-苯甲酰胺基团之间的电子流通。阴离子结合常数相对于不含分子内氢键的 *N*-苯甲酰胺基-*N'*-苯基硫脲高一个数量级,甚至在含水 15% 的乙腈溶液中仍能与阴离子有效结合。因此在基于硫脲基团的阴离子受体分子和有机催化剂的发展中,酰胺基团的引入可能具有积极的作用。在 *N*-苯甲酰胺基-*N'*-苯甲酰基硫脲分子中,由于两个苯环上取代基的改变对阴离子识别无影响,具有结构多样性的相应的脂肪族衍生物也将具有与之相类似的强的氢键结合能力。*N*-苯甲酰胺基-*N'*-苯甲酰基硫脲的分子结构的修饰当有助于拓展阴离子受体分子和有机催化剂研究的进一步发展。

关键词: 阴离子识别; 酰胺基硫脲; 氢键; 变构作用

Design and Synthesis of *N*-amidothiourea-Based Neutral Receptors for Anion Recognition

Abstract

Molecular recognition has played an important role in the field of supramolecular chemistry, and comprises cation, anion and neutral molecular recognition. The development of anion receptors was delayed compared with the cation receptors. It is therefore necessary to construct novel anion receptors. The anion recognition in nature is achieved through the cooperation of multiple hydrogen binding. So the development of neutral anion receptors based on hydrogen binding became the trend of anion receptors, especially the thiourea-based neutral anion receptors.

Thiourea has been a well known neutral binding site employed in the design of anion receptors. The thiourea-anion interaction is mainly hydrogen bonding. In order to increase its anion binding ability, the hydrogen bonding itself has been enhanced via structural modification and/or supplemented by other interactions such as additional hydrogen bonding and electrostatic interaction. *N*-alkyl and/or *N*-aryl substitution have been the main strategy hitherto employed to enhance hydrogen bonding by increasing the acidity of thioureido NH protons. With highly acidic thioureido NH protons, however, deprotonation may occur in the presence of anions. In case of incorporating in the receptor molecule more binding sites in addition to hydrogen bonding, sophisticated design of the receptor structures and appreciable synthesis efforts are required.

It was found from the previous work carried out in our lab that the anion-binding constants of *N*-benzamido-*N'*-phenylthioureas in MeCN were two orders of magnitude higher than those of the corresponding traditional *N*, *N'*-biphenylthioureas, despite lower acidity of the thioureido NH protons. And the anion binding constants of *N*-benzamido-*N'*-phenylthioureas, influenced by the substituents in the

N'-phenylthiourea moiety, showed less dependence on the substituents in the *N*-benzamido moiety. So we examined the aliphatic counterparts of *N*-benzamido-*N'*-phenylthioureas, *N*-amido-*N'*-phenylthioureas, to make the *N*-amido-*N'*-phenylthioureas a kind of more useful anion-binding site with more structural diversity.

This dissertation consists of five chapters.

In chapter 1, researches in the development of neutral anion receptors based on (thio)urea were reviewed. And the research proposal of this dissertation was presented based on the previous work in our lab.

Chapter 2 describes synthesis and characterization of *ca.* 30 receptors designed in this thesis for anion recognition. These receptors include *N*-amido-*N'*-phenylthiourea derivatives and *N*-benzamido-*N'*-benzoylthiourea derivatives. The equipments, materials and methods involved in this dissertation were also described.

The influence of anion on the absorbance of *N*-amido-*N'*-phenylthiourea derivatives is investigated in chapter 3. In *N*-amido-*N'*-phenylthioureas, it is more efficient to increase the anion binding constants by varying substituent in the *N'*-phenyl ring, and the variation of substituent in *N*-amido group had smaller influence on the acidity of NH protons and the anion binding constants. But it was found that the acidity of thioureido NH protons in *N*-amido-*N'*-phenylthioureas is lower than in *N*-benzamido-*N'*-phenylthioureas, yet the anion binding ability is higher. This makes the *N*-amidothiourea more useful receptor. It was concluded from NMR titrations that in MeCN it is hydrogen bonding between receptors and anions when the electron-withdrawing ability of the substituent in *N'*-phenyl is not higher than *m*-CF₃ or deprotonation when the substituent is *p*-NO₂. Compared with the receptors bearing no amido -NH proton, the hydrogen bonding network in the anion binding complexes of *N*-amido-*N'*-phenylthioureas favored the stabilization of NH protons and avoided the deprotonation. Because of the higher anion binding capacity and the formation of hydrogen bonding network in receptor-anion complexes, *N*-amido-*N'*-phenylthioureas can recognize CH₃CO₂⁻ in MeCN containing water up to 10% by volume.

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